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Abstract

Ar:O_2 low pressure plasma (Ar:O_2 LPP) surface treatment is proposed for increasing the surface energy and improve the adhesion of wood-polyethylene composite. The treatment time was varied between 20 and 90 s and the configuration of the shelves inside the plasma chamber (*direct* and *secondary downstream*) was also changed. Ar:O_2 LPP treatment during 30–40 s created new surface carbon–oxygen groups, increased the surface energy, mainly its polar component, reduced roughness and caused ablation of wood-polyethylene composite, irrespective of the configuration of the shelves inside the plasma chamber. The increase of the treatment time above 40 s did not cause additional surface modifications. Adhesion of the

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Keywords (separated by '-')	Wood-plastic composite (WPC) - Argon–oxygen low pressure plasma - Configuration of the plasma chamber - Surface treatment - Adhesion - Ageing
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ORIGINAL PAPER

Improved Surface and Adhesion Properties of Wood-Polyethylene Composite by Treatment with Argon–Oxygen Low Pressure Plasma

Andrés Jesús Yáñez-Pacios[1] · José Miguel Martín-Martínez[1]

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Abstract Ar:O_2 low pressure plasma (Ar:O_2 LPP) surface treatment is proposed for increasing the surface energy and improve the adhesion of wood-polyethylene composite. The treatment time was varied between 20 and 90 s and the configuration of the shelves inside the plasma chamber (*direct* and *secondary downstream*) was also changed. Ar:O_2 LPP treatment during 30–40 s created new surface carbon–oxygen groups, increased the surface energy, mainly its polar component, reduced roughness and caused ablation of wood-polyethylene composite, irrespective of the configuration of the shelves inside the plasma chamber. The increase of the treatment time above 40 s did not cause additional surface modifications. Adhesion of the wood-polyethylene composite was noticeably increased when was treated with Ar:O_2 LPP. The surface modifications of Ar:O_2 LPP treated wood-polyethylene composite were partially lost during 24 h after treatment.

Keywords Wood-plastic composite (WPC) · Argon–oxygen low pressure plasma · Configuration of the plasma chamber · Surface treatment · Adhesion · Ageing

Introduction

Wood plastic composites (WPCs) are used as substitute of wood materials in outdoor applications because of their higher ageing resistance and greater mechanical properties. WPCs are used in furniture, building and automotive industry, although their main applications are as materials for decking, railing, siding, and panelling with improved outdoor resistance.

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WPC is made of wood flour, polymer and additives (biocides, lubricants, ultraviolet stabilizers…) [1]. The polymer constitutes 30–70 wt% of WPC composition, polyethylene (PE), polypropylene (PP) and poly (vinyl chloride) (PVC) are the most common. The additives are added in about 5 wt% and they are used for imparting specific properties and improving compatibility between the polar wood material and the non-polar polymer [1]. During processing, the surface of WPC is enriched in polymer imparting relatively low surface energy, making it difficult to bond with adhesives or applying coatings. Nowadays, the joining of WPC material is mainly made by means of nails or by mechanical interlocking, this method is limited in WPC pieces with irregular geometrical shape. Alternatively, WPC material can be mechanically anchored to metallic structure [2], but the use of adhesives is not feasible due to its low surface energy. Furthermore, the application of coatings on WPC for being painted or decorated is not possible so dyes or colorants are currently added during WPC manufacturing.

In order to improve the adhesion of WPC to coatings, its low surface energy should be increased by means of surface treatments. Several physical and chemical surface treatments for different WPCs have been proposed in the literature [3], the surface treatment of WPC with flame, sanding, oxyfluorination, chromic acid and corona discharge are the most common [1, 4–7]. The most of those treatments caused notable improvement in adhesion properties of WPC, the most effective was the chromic acid treatment; however, due to environmental concerns, this treatment need to be substituted. The use of atmospheric pressure plasmas have been proposed for improving the polarity and adhesion properties of WPC. Thus, Moghadamzadeh et al. [7] have treated WPC made with high density polyethylene (PE) with corona discharge for improving its pull-off adhesion and the increased adhesion was ascribed to modifications of the surface roughness and the creation of new surface chemical groups. Similarly, Akhtarkhavari et al. [8] have found that the surface treatment of several WPCs by corona discharge caused adhesion improvement and paint ability. Other surface treatments with different atmospheric plasmas have been proposed for improving the surface properties of WPCs [9–11]. Wolkenhauer et al. [12] have used dielectric barrier discharge for improving the adhesion properties of different WPCs made with PE and they found an increase in surface energy caused by the surface chemical modifications produced by the treatment. Similar findings were obtained by Liu et al. [13] and Hünnekens et al. [14]. Surface treatments with atmospheric pressure plasmas have also been applied to WPC made with polypropylene (PP), high wettability and high adhesion were obtained [15, 16]. More recently, Yáñez-Pacios and Martín-Martínez [17, 18] proposed the surface treatment of different WPCs with atmospheric pressure plasma jet and UV/ozone, improved adhesion was obtained due to increased surface energy, modification of surface roughness and creation of new polar carbon–oxygen species. However, the surface modifications of WPC treated with atmospheric plasmas are lost in relatively short time after treatment (hydrophobic recovery) [19]. Hydrophobic recovery of non-polar materials can be better controlled by treatment with low pressure plasmas (LPPs) [20].

Air low pressure plasma (LPP) surface treatment of WPC has been proposed for improving its polarity [21] but the adhesion properties were not studied. Gupta et al. [22] have treated WPCs made with PE and PP with oxygen LPP and compared their effectiveness with other surface treatments (chromic acid, flame, benzophenone activated by UV irradiation), similar adhesion results were obtained although lower improvement in wettability and adhesion was obtained by using the treatment with benzophenone activated by UV irradiation. Air or oxygen LPP surface treatments produced ablation, crosslinking, chain scission, and surface roughening of polyethylene and WPC made with PE, and all these surface modifications were responsible of their improved adhesion [4, 21, 22].

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However, for substantial improvement in adhesion, WPC made with PE needs the treatment with oxygen LPP for 30 min and WPC made with PP should be treated for 10 min [22], the treatment times were high and different conditions were needed for WPCs made with different polymers.

It has been shown that the configuration of the plasma chamber during LPP treatment noticeably affected the extent of the surface modifications of rubber materials [23, 24]. The different configurations of the shelves in the plasma chamber allow different plasma species of distinct energy to reach the material surface, and different extent of surface modifications can be produced. For rubber materials, Henry el al. [24] have used *direct* and *downstream* air LPP configurations and Torregrosa-Coque et al. [23] have used *direct*, *etching* and *downstream* oxygen LPP configurations, and they found notably different surface modifications depending on the configuration of the shelves inside the plasma chamber. Thus, Henry et al. [24] have found the creation of new carbon–oxygen surface groups, improved wettability and decreased non-dispersive component of the surface energy on the rubber surface treated with *direct* air LPP during 2 min by using 20 W of power; however, the wettability was not modified by treating with *downstream* air LPP even for high discharge power. On the other hand, Torregrosa-Coque and Martín-Martínez [23] have also reported the creation of new carbon–oxygen species and noticeable decrease of ethylene glycol contact angle values on rubber surface treated with *direct* and *etching* oxygen LPP during less than 2 min, the adhesion was not improved due to migration of low-molecular species to the surface during LPP treatment. In order to avoid the migration of low molecular weight species to the surface and improving adhesion, Cantos-Delegido and Martín-Martínez [25] have treated rubber material with LPPs made with different mixtures of argon and oxygen, and they concluded that the treatment with LPP generated with Ar:O_2 (2:1, vol/vol) mixture in *direct* and *etching* configurations produced notable improvement in wettability and improved adhesion of vulcanized rubber material, the best conditions corresponded to 100–400 W power and short treatment times (60–800 s). By considering that the argon LPP treatment produces mainly ablation by ions bombardment of the surface [26] and that oxygen LPP treatment causes severe oxidation and surface functionalization [27], the use of argon + oxygen mixture may produce an adequate balance between surface modification and adhesion which may be beneficial for improving ageing resistance. However, to the best of our knowledge, the configuration of the plasma chamber during LPP treatment of WPC has not been considered yet in the existing literature.

In this study Ar:O_2 (2:1, vol/vol) LPP treatment for short time and by using different configurations of the shelves in the plasma reactor is proposed for improving the surface properties and adhesion of WPC made with PE, the stability of the surface modifications is monitored with time after treatment (ageing).

Experimental

Material

Commercial wood flour filled high density polyethylene composite (PE-WPC) made by extrusion in the form of alveolar boards was supplied by Condepols Company (Jaen, Spain). PE-WPC was cut into pieces of 3 × 7 cm^2 for LPP treatment and characterization.

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Surface Treatment with Low Pressure Plasma (LPP)

Radiofrequency (13.56 MHz) Digit Concept NT1 (BSET EQ, Antioch, CA, USA) plasma reactor was used to modify PE-WPC surface properties. The plasma was generated from a mixture of argon: oxygen (2:1, vol/vol). In previous recent study [25], the effectiveness of argon: oxygen (2:1, vol/vol) LPP was demonstrated, and this gas mixture was chosen in this study for balancing physical modifications and ablation and chemical modifications by oxidation on PE-WPC surface.

Two different shelves configurations were used in this study (Fig. 1): (1) *Secondary downstream*, in which PE-WPC sample is placed on the floating shelf located between the power and ground shelves; (2) *Direct,* in which PE-WPC sample is placed over the power shelf. PE-WPC is exposed directly to plasma in *direct* configuration, but indirectly in *secondary downstream* configuration.

Irrespective of the configuration of the shelves in the reactor, $Ar:O_2$ LPP treatment was carried out at 200 W of power, the treatment time was varied between 20 and 90 s, and the residual pressure into the reactor was 800 m Torr (1 kPa). Because of PE-WPC contains relatively significant amounts of moisture, the residual pressure used in this study during LPP treatment of PE-WPC is higher than usual [22, 23], and it was selected to create chemical and physical surface modifications without changing PE-WPC bulk composition.

Experimental Techniques

IR Spectroscopy

The chemical modifications in the PE-WPC surface produced by $Ar:O_2$ LPP treatment before and after ageing were assessed by attenuated total reflectance infrared spectroscopy

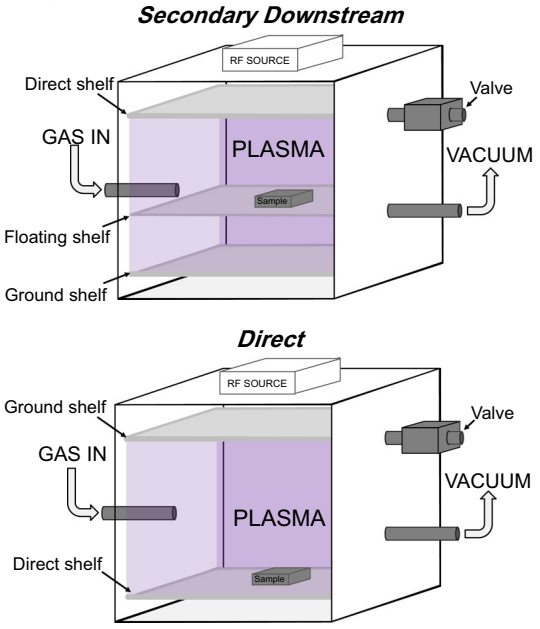

Fig. 1 Shelves configurations of LPP Digit Concept NT1 reactor

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(ATR-IR) in Alpha spectrometer (Bruker Optiks, Etlinger, Germany); Germanium prism was used. Sixty scans were averaged with a resolution of 4 cm^{-1}. The incidence angle of the IR beam was 45°. Under these experimental conditions, about 1 μm surface depth of AQ3 PE-WPC surface was analyzed.

Contact Angle Measurements

Contact angles were measured at 25 °C before and after ageing on as-received and Ar:O_2 LPP treated PE-WPC surface in Ramé-Hart 100 goniometer (Netcong, NJ, USA) and two different test liquids were used. 4 μl drops of bidistilled and deionised water (polar liquid) and diiodomethane (non-polar liquid) were placed on PE-WPC surface, and the contact angle values were measured immediately after drop deposition. The advancing and receding angles were measured by using the tilting plate method. Because of the contact angle values obtained by the sessile drop method agreed well with the advancing contact angle values, the advancing contact angle was considered as representative of the surface properties of WPC. At least five drops of each test liquid were placed on different locations of PE-WPC surface and the contact angle values on both sides of the drops were measured and averaged.

The surface energy (γ_S) and its polar (γ_S^p) and dispersive (γ_S^d) components of the as-received and Ar:O_2 LPP treated PE-WPC were obtained from the water and diiodomethane advancing contact angle values. Assuming that $\gamma_S = \gamma_S^p + \gamma_S^d$, the calculation of the polar and dispersive components of the surface energy of PE-WPC was carried out by using Owens–Wendt approach—Eq. (1):

$$(1 + \cos\theta_i)\left(\gamma_i^d + \gamma_i^p\right) = 2\left(\sqrt{\gamma_i^d \gamma_S^d} + \sqrt{\gamma_i^p \gamma_S^p}\right) \quad (1)$$

where γ_i is the surface tension of the test liquid used to measure the contact angle, θ_i is the advancing contact angle value, and the superscripts p and d mean the polar and dispersive components respectively of the surface tension of the test liquids or the surface energy of PE-WPC. The components of the surface tension of water were γ_{water}^p = 51 mN/m and γ_{water}^d = 21.8 mN/m, and the ones for diiodomethane were $\gamma_{CH_2I_2}^p$ = 0 mN/m and AQ4 $\gamma_{CH_2I_2}^d$ = 50.8 mN/m.

Scanning Electron Microscopy (SEM)

The changes of the surface topography of PE-WPC by treatment with Ar:O_2 LPP before and after ageing were assessed in Jeol JSM-840 microscope (Jeol Ltd., Tokyo, Japan) working at 15 kV. For improving contrast, PE-WPC surface was gold coated in Au/Pd Balzers metallizer SCD 004 (Oerlikon Surface Solutions, Balzers, Liechtenstein).

Adhesion Measurements

The changes in adhesion of PE-WPC by treatment with Ar:O_2 LPP before and after ageing were monitored by 180° peel tests of as-received or Ar:O_2 LPP treated PE-WPC/Magic Scotch® acrylic adhesive tape joints in TA-XT2i texture analyzer (Stable Micro Systems, Godalming, UK) by using a peeling rate of 10 mm/s (Fig. 2). Rectangular pieces of PE-WPC of dimensions 3 cm × 7 cm and pieces of Magic Scotch® tape (3 M, Minnesota, USA) of 18 cm × 1.9 cm were used. The adhesive tape was applied over the WPC surface

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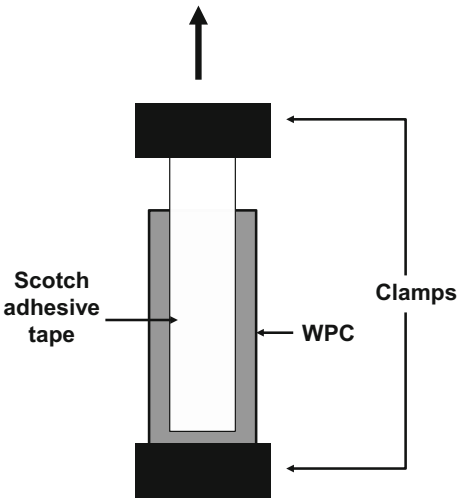

Fig. 2 Scheme of 180° peel adhesion test

and 30 consecutive passes with a rubber roller of 2 kg were carried out for allowing intimate contact between the PE-WPC surface and the adhesive tape. For facilitating the attachment of the adhesive joint to the upper clamp during 180° peel test, about 11 cm length of the adhesive tape was not joined to the PE-WPC. For adhesion test, the PE-WPC specimen was attached to the lower clamp and the adhesive tape was attached after being plied to the upper clamp (Fig. 2). Five replicates for each joint were carried out and averaged.

Results and Discussion

Optimization of Ar:O_2 LPP Surface Treatment of PE-WPC

In low pressure plasma reactor, the electric potential is applied between the power and the ground shelves, the power shelf has the highest electric potential in which all plasma species are created and concentrated. In the primary plasma mode (*direct* configuration) for generation of active plasma species, the materials are placed directly in the gas discharge, on or near the electrode plates of the reactor with full exposure to the working species of the plasma. Secondary plasma is typically used when a less intense plasma exposure is desired. Downstream secondary plasma (*secondary downstream* configuration) relies on the transfer of the active species (ions, electrons, radicals, and byproducts) from an upstream primary discharge to a secondary process chamber or sample placement area. Downstream secondary plasma contains the same types of active species as a primary discharge, but with lower kinetic energy and lower gas temperature [24]. Therefore, it can be anticipated that the LPP in *direct* configuration will create more extended surface modifications of PE-WPC placed on the power shelf, whereas the surface treatment in *secondary downstream* configuration, in which the PE-WPC is placed in a different shelf than the power shelf, will be exposed to softer non-equilibrium plasma with lower ion density, and thus less aggressive surface modifications can be expected.

Figure 3a, b show two different regions of the ATR-IR spectra of the as-received and Ar:O_2 LPP treated PE-WPC in *secondary downstream* shelves configuration (*downstream*

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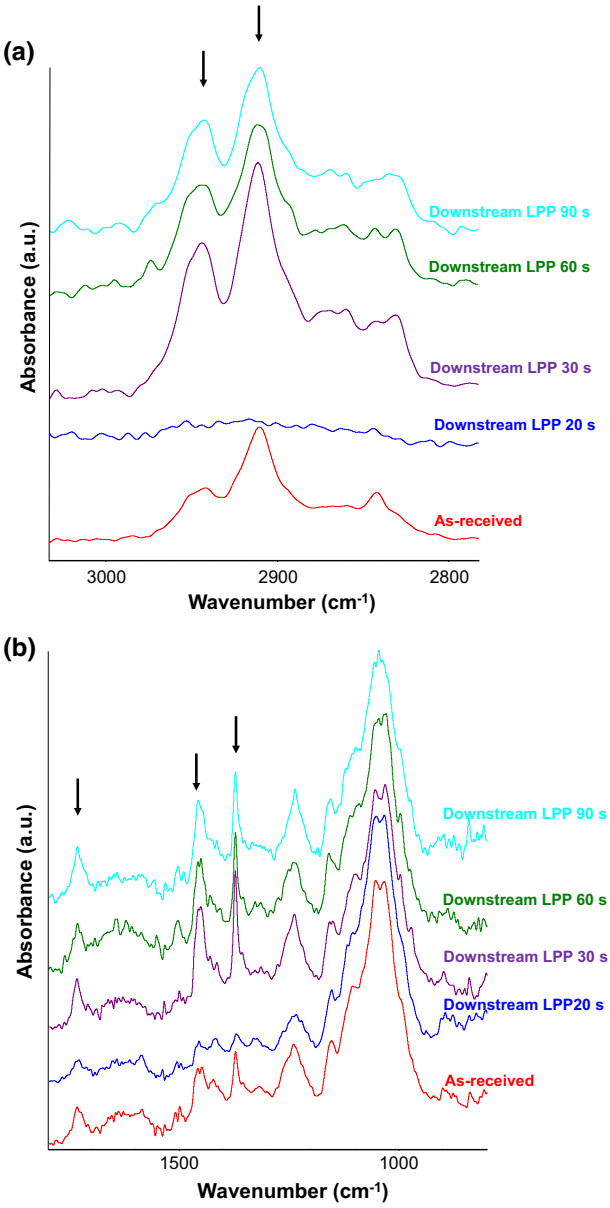

Fig. 3 ATR-IR spectra of the as-received and Ar:O_2 LPP (*secondary downstream*) treated PE-WPC for different times. **a** Region of 3000–2800 cm^{-1}. **b** Region of 1750–800 cm^{-1}. Germanium prism

LPP) between 20 and 90 s. The ATR-IR spectrum of PE-WPC shows typical bands due to lignocellulosic material—broad stretching band of OH groups at 3340 cm^{-1}, stretching C=O bands at 1633 and 1740 cm^{-1}, hydroxyl group band at 1023 cm^{-1} (the most intense)—and polyethylene –C–H stretching bands at 2842–2950 cm^{-1}, C–H bending bands at 1375 and 1455 cm^{-1} [28]. By considering that the relative intensity of the band of hydroxyl groups at 1023 cm^{-1} is higher than the one of the methylene groups at 2912 cm^{-1}, PE-WPC surface has relatively important amount of wood content.

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Mild treatment of wood-polyethylene composite with Ar:O_2 LPP (*downstream*) for 20 s AQ5 decreases the intensity of the C–H stretching bands at 2838–2949 cm^{-1} (Fig. 3a) and the C–H bending bands at 1376–1454 cm^{-1} (Fig. 3b) due to methylene groups of polyethylene, and the intensity of the C=O band due to wood material decreases, suggesting that ablation of PE-WPC surface is produced. However, the increase of the Ar:O_2 LPP (*downstream*) treatment time to 30 s rises the intensity of the bands at 2838–2949 cm^{-1} (Fig. 3a) and 1376–1454 cm^{-1} (Fig. 3b) corresponding to polyethylene, indicating the enrichment in polymer of PE-WPC surface; furthermore, the Ar:O_2 LPP (*downstream*) treatment for 30 s increases the intensity of the stretching C=O band at 1733 cm^{-1} (Fig. 3b) because of surface oxidation of PE-WPC is produced and new carbon–oxygen species are formed. The increase of the Ar:O_2 LPP (*downstream*) treatment time above 30 s shows similar ATR-IR spectra, indicating that the effectiveness of the treatment is not increased because of no additional surface modifications are produced. According to the literature [4, 21, 22] oxygen or air low pressure plasma treatment of wood plastic composites also creates new C–O groups, similarly to the surface treatment of PE-WPC with Ar:O_2 LPP.

Figure 4a, b show two different regions of the ATR-IR spectra of the as-received and Ar:O_2 LPP treated PE-WPC in *direct* shelves configuration (*direct* LPP) between 20 and 90 s. Because of PE-WPC is exposed to the just generated plasma species, it can be expected that the Ar:O_2 LPP (*direct*) treatment be more aggressive than Ar:O_2 LPP (*downstream*) one. Ar:O_2 LPP (*direct*) treatment of PE-WPC for 20 and 30 s decreases the intensity of the C–H stretching bands at 2838–2949 cm^{-1} (Fig. 4a) and the C–H bending bands at 1376–1454 cm^{-1} (Fig. 4b) of polyethylene, and the intensity of the C=O band due to wood material decreases, the surface ablation of the composite is produced. Similar surface modifications are obtained by treatment of PE-WPC with Ar:O_2 LPP (*downstream*) for 20 s; however, when the treatment time increases to 30 s, surface oxidation is not produced in PE-WPC treated with Ar:O_2 LPP (*direct*). When the Ar:O_2 LPP (*direct*) treatment of PE-WPC is carried out for 40 s, the intensity of the bands of polyethylene at 2838–2949 cm^{-1} (Fig. 4a) and 1376–1454 cm^{-1} (Fig. 4b) increases, indicating the enrichment in polymer or the removal of wood fibers in the PE-WPC surface, and furthermore an increase of the intensity of the stretching C=O band at 1733 cm^{-1} (Fig. 4b) is obtained because of surface oxidation of PE-WPC is produced and new carbon–oxygen species are formed. The increase of the Ar:O_2 LPP (*direct*) treatment time above 40 s shows similar ATR-IR spectra but the intensity of the C=O bands is lower suggesting that less noticeable removal of wood fibers and lower degree of oxidation is produced, i.e., the ablation is dominant over the oxidation of PE-WPC surface.

According to the evidences provided by ATR-IR spectroscopy, the optimal surface modifications of Ar:O_2 LPP treated PE-WPC are obtained by treatment during 30 s in *secondary downstream* configuration or during 40 s in *direct* configuration, the effects of the Ar:O_2 LPP treatment are less marked by using longer treatment time. The creation of new polar groups on Ar:O_2 LPP treated PE-WPC surface should improve its surface energy. Figure 5 shows the variation of the surface energy of Ar:O_2 LPP treated PE-WPC in *secondary downstream* and *direct* configurations as a function of the treatment time. The surface energy of the as-received PE-WPC is 39 mJ/m^2 (it is shown as dotted line in Fig. 5), the dispersive component is the only one contributing to the surface energy, indicating that the outermost surface of the composite is mostly enriched in polyethylene. The surface energy of PE-WPC increases to 54–57 mJ/m^2 by Ar:O_2 LPP treatment for 20 s only and more noticeable increase is produced by increasing the treatment time up to 30–40 s, the surface energy is not varying by further increasing of the treatment time.

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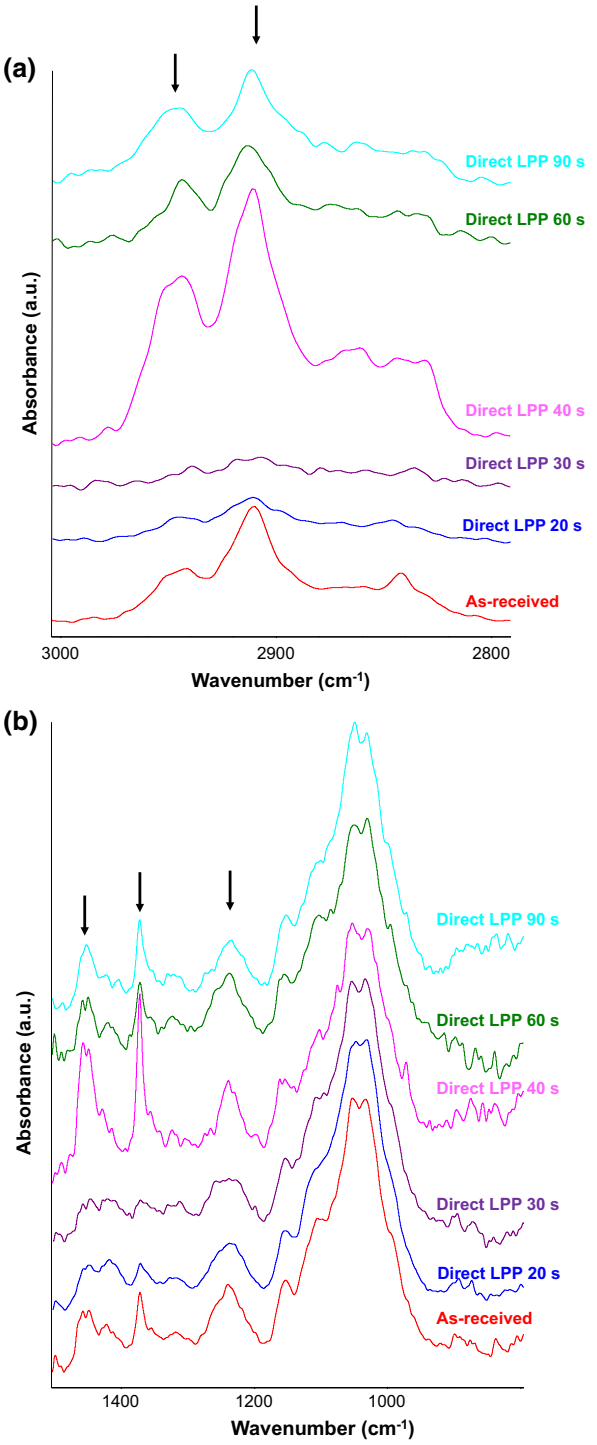

Fig. 4 ATR-IR spectra of the as-received and Ar:O_2 LPP (*direct*) treated PE-WPC for different times. **a** Region of 3000–2800 cm^{-1}. **b** Region of 1500–800 cm^{-1}. Germanium prism

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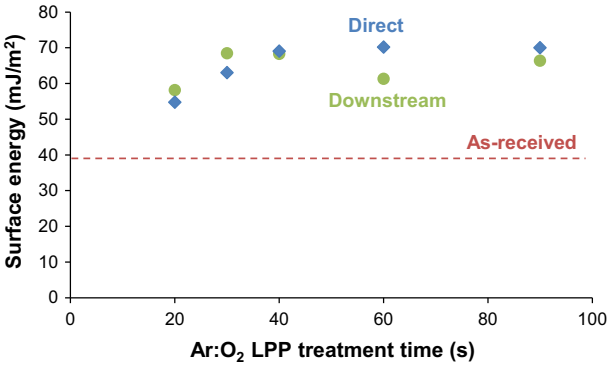

Fig. 5 Variation of the surface energy of Ar:O_2 LPP (*direct* and *secondary downstream*) treated PE-WPC as a function of the treatment time

Similar variations in the surface energy of PE-WPC are obtained by using *secondary downstream* and *direct* configurations, a value of 70 mJ/m^2 is reached, i.e. twofold increase in surface energy is produced in Ar:O_2 LPP treated PE-WPC.

Figure 6 shows as representative example the variation of the surface energy and their dispersive and polar components as a function of the treatment time for Ar:O_2 LPP (*direct*) treated PE-WPC. Ar:O_2 LPP (*direct*) treatment for 20 s decreases slightly the dispersive component of the surface energy of the as-received PE-WPC and an important increase of the polar component of the surface energy is produced; the increase of the treatment time does not change the dispersive component of the surface energy of PE-WPC surface but an increase in the polar component is produced up to treatment time of 40 s, not varying by further increase of the treatment time. Therefore, the creation of new carbon–oxygen polar groups in Ar:O_2 LPP (*direct*) treated PE-WPC produces an increase in the polar component of the surface energy, the maximum value is produced by treatment during 40 s; for longer treatment time, the surface energy of PE-WPC does not change. On the other hand, the Ar:O_2 LPP (*direct*) treatment decreases slightly the dispersive component of the surface energy of PE-WPC likely due to ablation which should be evidenced by changes in the surface topography.

The changes in the topography of PE-WPC by treatment with Ar:O_2 LPP were evidenced by SEM. Figure 7 shows the SEM micrographs of the as-received and Ar:O_2 LPP treated PE-WPC for different treatment times. As-received PE-WPC shows rough topography and the surface is enriched in polyethylene (Fig. 7). The treatment with Ar:O_2 LPP

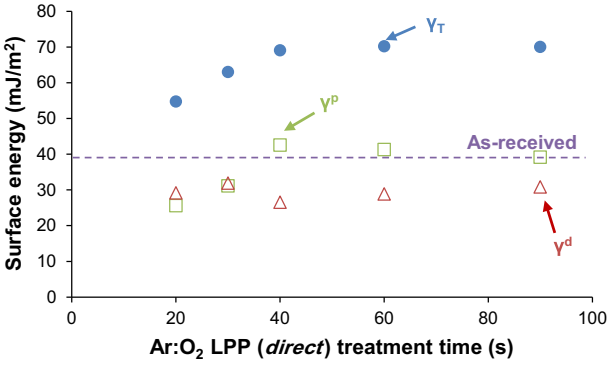

Fig. 6 Variation of the surface energy (γ_T) and their polar (γ^p) and dispersive (γ^d) components of Ar:O_2 LPP (*direct*) treated PE-WPC as a function of the treatment time. Dashed line corresponds to the total surface energy of as-received PE-WPC

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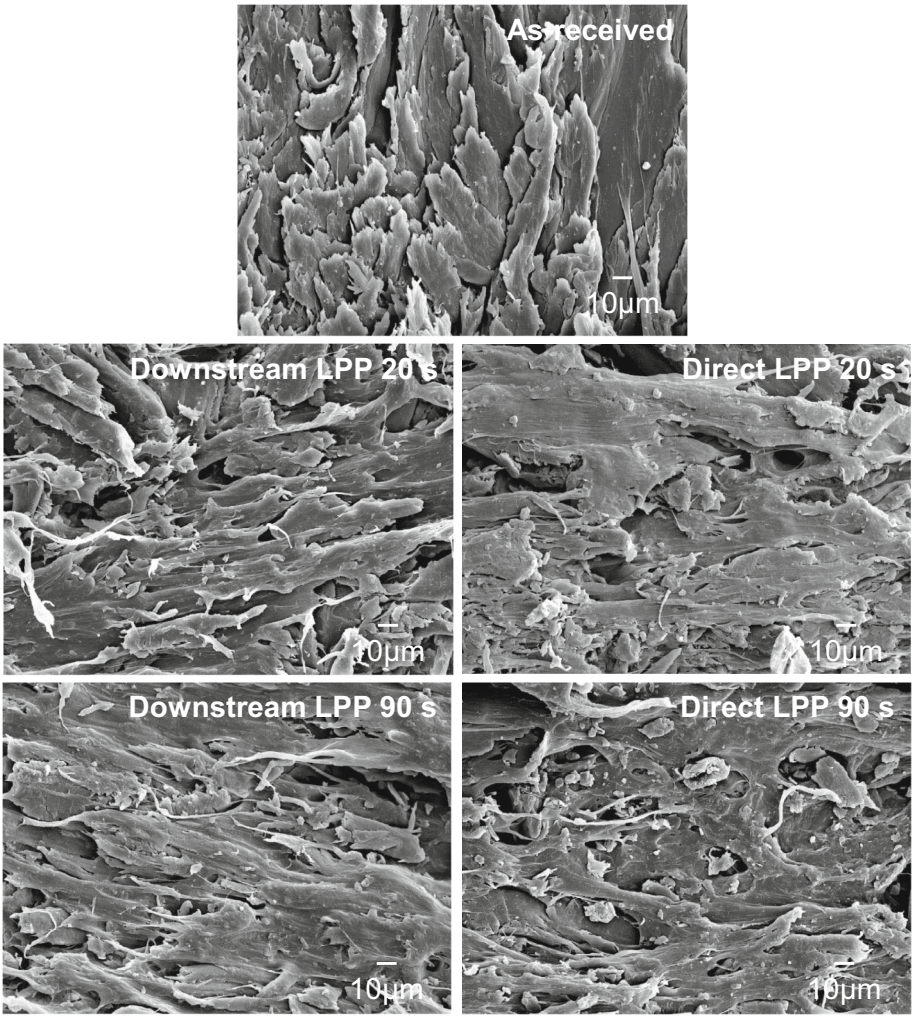

Fig. 7 SEM micrographs of the as-received and Ar:O_2 LPP (direct and secondary downstream) treated PE-WPC for different times

for 20 s only changes the topography of PE-WPC producing ablation and smoothening of the surface, and an enrichment in polyethylene, somewhat more markedly by treatment with Ar:O_2 LPP (*direct*). The increase of the treatment time enhances the ablation and somewhat similar topographies are obtained in PE-WPC surface treated with Ar:O_2 LPP, the surface topography is similar in the composite treated with Ar:O_2 LPP (*direct*) and (*secondary downstream*) for 90 s. These results agree well with the findings of ATR-IR spectroscopy and surface energy, as the more noticeable surface modifications are produced by treatment of PE-WPC with Ar:O_2 LPP for 30–40 s.

Figure 8 shows the variation of the 180° peel strength of as-received and Ar:O_2 LPP treated PE-WPC/Scotch® tape joints as a function of the treatment time. The adhesion of the joint made with the as-received PE-WPC is low (55 N/m) and it is always increased when Ar:O_2 LPP treatment is applied. Slight increase in 180° peel strength is obtained in

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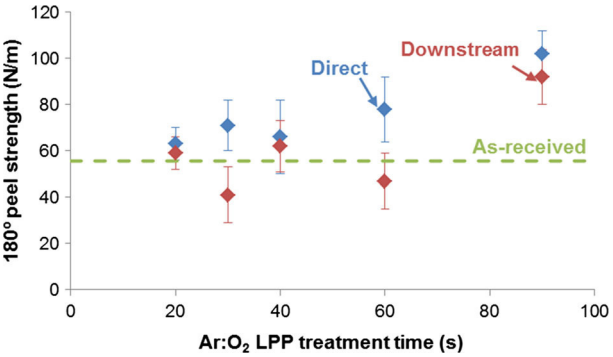

Fig. 8 Variation of the 180° peel strength of Ar:O_2 LPP treated PE-WPC/Magic Scotch® tape adhesive joints as a function of the treatment time. All joints show an adhesion failure

the joints made with Ar:O_2 LPP treated PE-WPC for 20 s only, irrespective of the configuration of the shelves in the plasma chamber (*direct* or *secondary downstream*), the increase is due to the increase in surface energy, mainly of its polar component, ablation, removal of roughening, and creation of new polar groups. 180° peel strength increases moderately by increasing the Ar:O_2 LPP treatment time, the adhesion is slightly higher by using *direct* configuration. Interestingly, the highest 180° peel strength corresponds to the joints made with Ar:O_2 LPP treated PE-WPC for 90 s [92 N/m for Ar:O_2 LPP (*downstream*) and 102 N/m for Ar:O_2 LPP (*direct*)]. This increase can be ascribed to the creation of some porosity on the treated PE-WPC surface that is evidenced in the SEM micrographs (Fig. 7) which may favour the mechanical interlocking of the acrylic adhesive with the treated PE-WPC surface.

Durability of Ar:O_2 LPP (*direct*) Treated PE-WPC

The durability of the Ar:O_2 LPP treated PE-WPC surface was monitored as a function of the time (from 1 h up to 2 years) in open air (24 °C and 40% relative humidity). Because of the highest 180° peel strength was obtained in the joints made with PE-WPC treated with Ar:O_2 LPP (*direct*) for 90 s, these conditions were selected for monitoring the extent of ageing.

The variations in the chemical composition with the time of Ar:O_2 LPP (*direct*) treated PE-WPC were monitored by ATR-IR spectroscopy. Figure 9 shows the ATR-IR spectra of Ar:O_2 LPP (*direct*) treated PE-WPC after being exposed to open air between 1 h and 14 days. One hour after Ar:O_2 LPP (*direct*) treatment, the intensity of the broad band at 3300 cm^{-1} due to OH stretching decreases with respect to the intensity of the C–H stretching bands at 2838–2949 cm^{-1}, indicating the enrichment in polyethylene of PE-WPC surface: the increase of the time in open air up to 24 h gradually decreases more the intensity of the broad OH stretching band at 3300 cm^{-1}, indicating gradual loss of polar groups in PE-WPC with the time. The increase of the time above 24 h does not show noticeable changes in the ATR-IR spectra of Ar:O_2 LPP (*direct*) treated PE-WPC, indicating stabilization of the surface chemistry. Therefore, the increase of the time after Ar:O_2 LPP (*direct*) treatment affects the chemical composition of PE-WPC surface.

The increase of the time after Ar:O_2 LPP (*direct*) treatment of PE-WPC also affects its surface energy and their dispersive and polar components. Figure 10 shows the variation of

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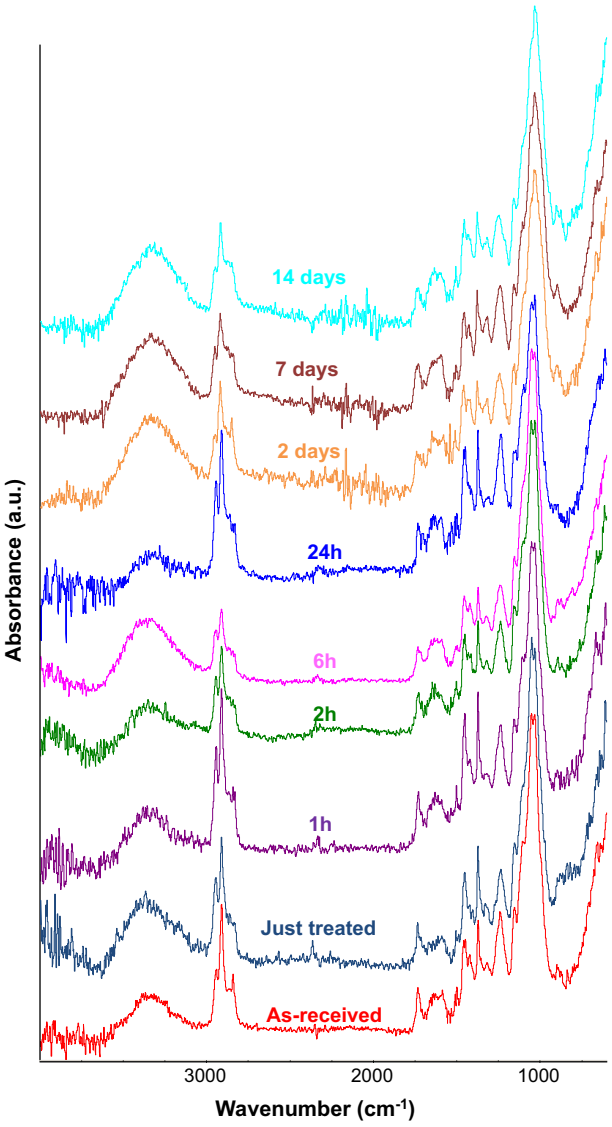

Fig. 9 ATR-IR spectra of the as-received and Ar:O_2 LPP (*direct*) treated PE-WPC for 90 s at different times after treatment. Germanium prism

the surface energy and their components of Ar:O_2 LPP (*direct*) treated PE-WPC as a function of the time after treatment. Whereas the dispersive component of the surface energy is not affected by the time after Ar:O_2 LPP (*direct*) treatment, 1 day after treatment the surface energy of Ar:O_2 LPP (*direct*) treated PE-WPC decreases from 70 mJ/m^2 in the just treated PE-WPC to 63 mJ/m^2 after 1 day, and it is maintained constant for longer times. The decrease in surface energy of Ar:O_2 LPP (*direct*) treated PE-WPC with the time after treatment can be ascribed to the decrease in the polar component, in agreement with the evidences shown by ATR-IR spectroscopy. However, even the surface energy decreases with the time after treatment, after 7 days the surface energy of Ar:O_2 LPP (*direct*) treated PE-WPC after 7 days is 60 mJ/m^2, which is substantially higher than the

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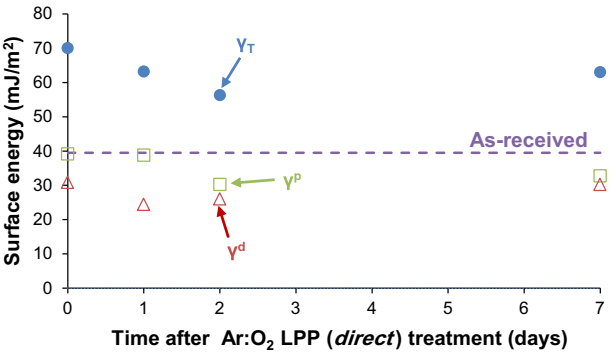

Fig. 10 Variation of the surface energy (γ_T) and their polar (γ^p) and dispersive (γ^d) components of Ar:O_2 LPP (*direct*) treated PE-WPC for 90 s as a function of the time after treatment (ageing time)

one of the as-received PE-WPC indicating a reasonable durability of the treatment over the time.

With respect to the variations of the surface topography of Ar:O_2 LPP (*direct*) treated PE-WPC with the time after treatment, Fig. 11 shows that is maintained even up to 2 years.

Finally, the variation of the 180° peel strength of Ar:O_2 LPP (*direct*) treated PE-WPC/Magic Scotch® adhesive tape joints was monitored as a function of the time after treatment. The joints were made with Ar:O_2 LPP (*direct*) treated PE-WPC exposed to open air at different times after treatment. Figure 12 shows an important decrease in 180° peel strength in the joints made with Ar:O_2 LPP (*direct*) treated PE-WPC produced after 1 day of treatment, which can be expected because of the loss of polar groups evidenced in the ATR-IR spectra and the decrease in the surface energy shown in Fig. 10. The increase of the time after treatment between 1 and 7 days maintains the 180° peel strength, in agreement with the evidences provided by ATR-IR spectroscopy and surface energy measurements, indicating the existence of hydrophobic recovery. Therefore, additional studies should be carried out for inhibiting the hydrophobic recovery in LPP treated PE-WPC materials. Therefore, the Ar:O_2 LPP treatment of PE-WPC during short time is efficient and acceptably stable over the time and it is promising for improving the adhesion and paint-ability of wood-plastic composites.

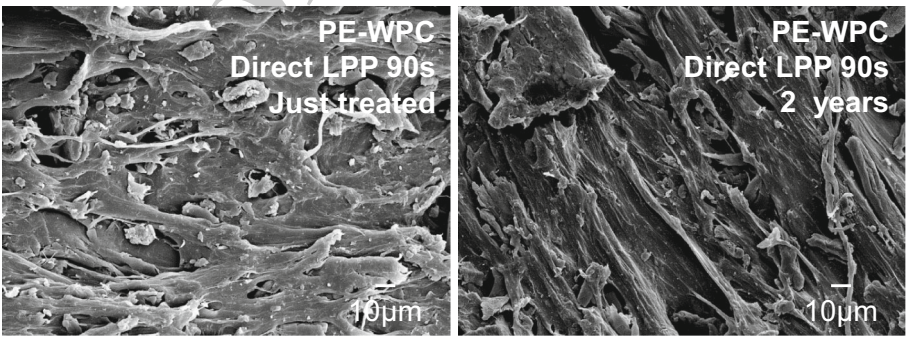

Fig. 11 SEM micrographs of Ar:O_2 LPP (*direct*) treated PE-WPC for 90 s immediately and 2 years after treatment

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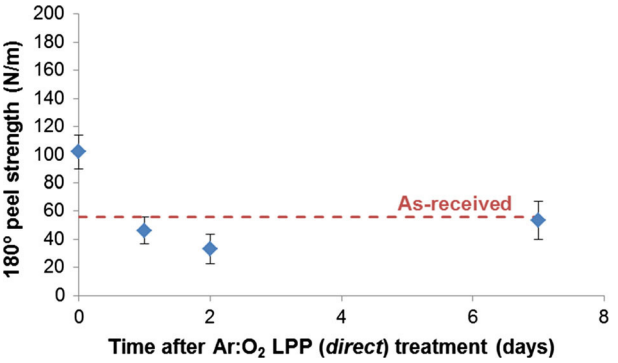

Fig. 12 Variation of the 180° peel strength of Ar:O_2 LPP treated PE-WPC (90 s)/Magic Scotch® tape adhesive joints as a function of the time after treatment (ageing time). All joints show an adhesion failure

Conclusions

Ar:O_2 LPP treatment for less than 90 s in *direct* and *secondary downstream* configurations of the shelves in the plasma chamber changed the surface chemistry, surface energy, topography and adhesion of PE-WPC. Ar:O_2 LPP treatment created new carbon–oxygen polar moieties on PE-WPC surface which are responsible of the increase in surface energy, mainly of its polar component; furthermore, the Ar:O_2 LPP treatment removed roughness and produced ablation on PE-WPC surface. These effects are maximal for Ar:O_2 LPP treatment for 30–40 s, the increase of the treatment time did not modify substantially the surface properties of PE-WPC irrespective of *direct* and *secondary downstream* configurations of the shelves in the plasma chamber. Because of the surface modifications produced on PE-WPC, the 180° peel strength of joints made with Ar:O_2 LPP treated PE-WPC increased two-fold with respect to the one made with the as-received composite. The durability of Ar:O_2 LPP treated PE-WPC was acceptable because of the chemical modifications on the surface were partially lost during 24 h after treatment, and a slight decrease in the surface energy (mainly of the polar component) was produced; no noticeable changes in Ar:O_2 LPP treated PE-WPC surface was produced for times higher than 1 day. Finally, 180° peel strength value of the joints made with Ar:O_2 LPP treated PE-WPC decreased during 24 h after treatment.

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References

1. Gramlich WM, Gardner DJ, Neivandt DJ (2006) Surface treatments of wood-plastic composites (WPC) to improve adhesion. J Adhes Sci Technol 20:1873–1887
2. Kraus E, Baudrit B, Heidemeyer P, Bastian M, Stoyanov OV, Starostina IA (2015) Problems in adhesion bonding of WPC. Polym Res J 9:327–335
3. Ryntz RA (1998) Adhesion to plastics: molding and paintability, 1st edn. Global Press, Chicago, p 112. ISBN 978-1890086022
4. Gupta BS, Laborie M-PG (2007) Surface activation and adhesion properties of wood-fiber reinforced thermoplastic composites. J Adhes 83:939–955

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Article No. : 9899 | LE | TYPESET
MS Code : PCPP-18-AM-0015 | CP | DISK

5. Dimitriou A, Hale MD, Spear MJ (2016) The effect of four methods of surface activation for improved adhesion of wood polymer composites (WPC). Int J Adhes Adhes 68:194–816
6. Oporto GS, Gardner DJ, Bernhardt G, Neivandt DJ (2007) Characterizing the mechanism of improved adhesion of modified wood plastic composite (WPC) surfaces. J Adhes Sci Technol 21:1097–1116
7. Moghadamzadeh H, Rahimi H, Asadollahzadeh M, Hemmati AR (2011) Surface treatment of wood polymer composites for adhesive bonding. Int J Adhes Adhes 31:816–821
8. Akhtarkhavari A, Kortschot MT, Spelt JK (2004) Adhesion and durability of latex paint on wood fiber reinforced polyethylene. Prog Org Coat 49:33–41
9. Di M, Liu Y (2011) Stability and ageing of plasma treated wood/polyethylene composites surfaces. Adv Mat Res 150–151:829–833
10. Tao Y, Di M (2011) Study on plasma treatment and adhesion of wood/polyethylene composites. Appl Mech Mater 66–68:911–915
11. Tao Y, Wang H, Di M (2012) Evolution of surface properties for plasma treated wood/polyethylene composites under water soaking. Mater Eng 2:94–98
12. Wolkenhauer A, Avramidis G, Hauswald E, Militz H, Viöl W (2008) Plasma treatment of wood-plastic composites to enhance their adhesion properties. J Adhes Sci Technol 22:2025–2037
13. Liu Y, Tao Y, Lv X, Zhang Y, Di M (2010) Study on the surface properties of wood/polyethylene composites treated under plasma. Appl Surf Sci 257:1112–1118
14. Hünnekens B, Peters F, Avramidis G, Krause A, Militz H, Viöl W (2016) Plasma treatment of wood-polymer composites: a comparison of three different discharge types and their effect on surface properties. J App Polym Sci 133(1–9):43376
15. Oporto GS, Gardner DJ, Bernhardt G, Neivandt DJ (2009) Forced air plasma treatment (FAPT) of hybrid wood plastic composite (WPC)-fiber reinforced plastic (FRP) surfaces. Compos Interfaces 16:847–867
16. Hämäläinen K, Kärki T (2013) Effects of atmospheric plasma treatment on the surface properties of wood-plastic composites. Adv Mater Res 718–720:176–185
17. Yáñez-Pacios AJ, Martín-Martínez JM (2017) Surface modification and improved adhesion of wood-plastic composites (WPC) made with different polymers by treatment with atmospheric pressure rotating plasma jet. Int J Adhes Adhes 77:204–213
18. Yáñez-Pacios AJ, Martín-Martínez JM (2017) Surface modification and adhesion of wood-plastic composite (WPC) treated with UV/ozone. Compos Interfaces 25:127–149
19. Hünnekens B, Krause A, Militz H, Viöl W (2017) Hydrophobic recovery of atmospheric pressure plasma treated surfaces of Wood-Polymer Composites (WPC). Eur J Wood Prod 75:761–766
20. Butrón-García MI, Jofre-Reche JA, Martín-Martínez JM (2015) Use of statistical design of experiments in the optimization of Ar–O_2 low-pressure plasma treatment conditions of polydimethylsiloxane (PDMS) for increasing polarity and adhesion, and inhibiting hydrophobic recovery. Appl Surf Sci 332:1–11
21. Constantinescu G, Totolin M, Cojocariu A, Popa VI, Vasile C (2007) Study of the surface properties of some polyolefin/lignocellulosic composites treated by plasma. Cell Chem Technol 41:463–472
22. Sanchis MR, Blanes V, Blanes M, Garcia D, Balart R (2006) Surface modification of low density polyethylene (LDPE) film by low pressure O_2 plasma treatment. Eur Polym J 42:1558–1568
23. Torregrosa-Coque R, Martín-Martínez JM (2011) Influence of the configuration of the plasma chamber on the surface modification of synthetic vulcanized rubber treated with low-pressure oxygen RF plasma. Plasma Process Polym 8:1080–1092
24. Henry A, Vallat MF, Noël C, Belmonte T, Roucoules V (2015) Influence of plasma chamber set-up on the surface modification of non-vulcanized and pure SBR rubber treated at radio-frequencies air plasma. Plasma Process Polym 12:1139–1152
25. Cantos-Delegido B, Martín-Martínez JM (2015) Treatment with Ar–O_2 low-pressure plasma of vulcanized rubber sole containing noticeable amount of processing oils for improving adhesion to upper in shoe industry. J Adhes Sci Technol 29:1301–1314
26. Castro-Vidaurre EF, Achete CA, Gallo F, Garcia D, Simão R, Habert AC (2002) Surface modification of polymeric materials by plasma treatment. Mater Res 5:37–41
27. Vesel A, Mozetič M (2016) In: Izdebska J, Thomas S (eds) Low pressure plasma-assisted polymer surface modifications. Printing on polymers. William Andrew, Elsevier, New York
28. Stark NM, Matuana LM (2004) Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. Polym Degrad Stab 86:1–9

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